COORDINATION COMPOUNDS

BONDING IN COORDINATION COMPOUNDS

BONDING IN COMPLEXES

VALENCE BOND THEORY

Pauling is the credited developer of this theory. Below, we have outlined the key aspects of the theory.

- (i) When subjected to the impact of strong field ligands, the electrons of the central metal ion may be compelled to pair up, contrary to the Hund's rule of maximum multiplicity.
- (ii) In the presence of weak field ligands, the electronic configuration of the central metal atom/ion remains unaltered.
- (iii) If the complex harbors unpaired electrons, it exhibits paramagnetic behavior. Conversely, if it lacks unpaired electrons, it displays diamagnetic characteristics, and its magnetic moment is computed using the spin-only formula.

Magnetic moment (μ) = $\sqrt{n(n+2)}BM$

where n is the number of unpaired electrons in the metal ion.

Relation between unpaired electrons and magnetic moment

Magnetic moment (Bohr magnetons)	0	1.73	2.83	3.87	4.90	5.92
Number of unpaired electrons	0	1	2	3	4	5

Thus, the knowledge of the magnetic moment can be of great help in ascertaining the type of complex.

(iv) When ligands are arranged in increasing order of their splitting power then an experimentally determined series is obtained named as spectrochemical series.

> < EDTA < $NH_3 \approx py$ < en < dipy < phen < NO_2 ^{[[]]-}CN⁻ < CO ______ Strong field ligands ______]

- (v) The central metal ion possesses a set of vacant orbitals designed to accommodate electrons contributed by the ligands. The count of these empty orbitals matches the coordination number of the metal ion in a given complex.
- (vi) The atomic orbitals (s, p, or d) of the metal ion undergo hybridization, giving rise to hybrid orbitals endowed with specific directional characteristics. These hybrid orbitals then accept electron pairs from ligands to establish coordination bonds.
- (vii) The d-orbitals involved in this hybridization process can be either the inner (n − 1) d orbitals or the outer n d-orbitals. Complexes formed through these two methods are respectively termed inner orbital complexes and outer orbital complexes.

Following table provides the types of hybridization with different coordination number.

Coordination	Type of	Shape of complex
number of metal	hybridization	
4	sp ³	Tetrahedral
4	dsp ²	Square planer
5	sp ³ d	Trigonal
		bipyramidal
6	Sp ³ d ²	Octahedral
6	d ² sp ³	Octahedral

It's worth emphasizing that the anticipation of metal hybridization and the shape of the complex can be made more accessible when certain attributes of the complex, such as its magnetic properties, geometry, or the presence of isomerism, are known. **Coordination Number Six.**

In the diamagnetic octahedral complex, $[Co (NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration represented as shown below.

Chemistry

$[Co(NH_3)_6]^{3+}$

(inner orbital or low spin complex)

d²sp³ hybrid orbital Six pairs of electrons from six NH₃ molecules.

Consequently, the complex adopts an octahedral geometry and displays diamagnetic properties due to the absence of unpaired electrons. Given that the formation of the complex involves the hybridization of the inner d-orbital (3d), it is classified as an inner orbital complex, or alternatively, a low spin or spin-paired complex.

The complex $[FeF_6]^{4-}$ is paramagnetic and uses outer orbital (4d) in hybridization (sp^3d^2) ; it is thus called as outer orbital or high spin or spin free complex. So,



Six pairs of electrons from six F⁻ ions.

Coordination Number Four:

Within the paramagnetic tetrahedral complex [NiCl₄]^{2–}, nickel exists in a +2 oxidation state with an electronic configuration of 3d⁸. The hybridization scheme is as shown in figure.



sp³ hybrid orbitals

Four pairs of electrons from four Cl⁻ ions. The compound is paramagnetic since it contains two unpaired electrons.

Similarly complex [Ni (CO)₄] has tetrahedral geometry and is diamagnetic as it contains no unpaired electrons. The hybridization scheme is as shown in figure.

Class-12th



sp³ hybrid orbitals

Four pairs of electrons from four CO molecules. Complexes of Pd (II) and Pt (II) are usually four-coordinate, square planar, and diamagnetic and this arrangement is often found for Ni (II) complexes as well, e.g., in [Ni (CN)₄]^{2–} (here nickel is in +2 oxidation state and has electronic configuration $3d^8$). Since the free ion is in the ground state in both scenarios, they are both paramagnetic. The bonding description must encompass electron pairing and ligand-metal-ligand bond angles of 90^o. This is achieved through the hybridization of one (n–1) d, one ns, and two np orbitals, forming four equivalent dsp² hybrid orbitals directed towards the corners of a square. These hybrid orbitals then engage in covalent σ bonds with the ligands, with the bonding electron pairs contributed by the ligands. The hybridization scheme for [PtCl₄]^{2–} is as shown in figure.



dsp² hybrid orbitals Four pairs of electrons from four Cl[–] ions.

Similarly the hybridization scheme for $[Ni(CN)_4]^{2-}$ is as shown in figure.



Four pairs of electrons from four CN⁻ ions.

It is found that $[Cu(NH_3)_4]^{2+}$ is square planar and paramagnetic with one unpaired electron in 4p-orbital. The hybridization scheme is as follow.



dsp² hybrid orbitals

Four pairs of electrons from four $\ensuremath{\mathsf{NH}}_3$ molecules.

Note. [Ni (CN)₅]³⁻ is determined to exhibit diamagnetism, and it features two distinct Ni – C bond lengths. Specifically, four of these bond lengths are equivalent, while the fifth one differs. The hybridization pattern for [Ni (CN)₅]³⁻ is illustrated in the provided figure.



dsp³ hybrid orbitals

Five lone pairs of electrons from five CN⁻-ions



square pyramidal.

While the valence bond theory effectively describes the formation, structures, and magnetic properties of coordination compounds,

it suffers from the following shortcomings:

- 1. Several assumptions underlie this theory.
- 2. Magnetic data lacks a quantitative interpretation.

- 3. This theory does not address the spectral (color) characteristics of coordination compounds.
- 4. It does not offer a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- 5. It does not make precise predictions concerning the structures of 4-coordinate complexes, be they tetrahedral or square-planar.
- 6. It does not differentiate between strong and weak ligands.

CRYSTAL FIELD THEORY (CFT)

Crystal field theory is currently more widely embraced compared to valence bond theory. It posits that the interaction between the central metal and ligands in a complex is purely electrostatic. The central metal, forming a cation within the complex, carries a positive charge corresponding to its oxidation state. This metal cation is surrounded by negatively charged ligands or neutral molecules with lone pairs of electrons. If the ligand is a neutral molecule like NH3, the negative end of its dipole points towards the metal cation. The electrons on the central metal experience repulsive forces from those on the ligands, causing them to avoid the direction of ligand approach.

Crystal field theory makes several key assumptions:

- Ligands are treated as point charges.
- > There is no interaction between the metal orbitals and ligand orbitals.
- All d orbitals on the metal possess the same energy (i.e., they are degenerate) in the isolated atom. However, when a complex is formed, the degeneracy of these orbitals is disrupted, resulting in different orbital energies. In a gaseous isolated metal ion, all five d orbitals have identical energy and are considered degenerate. But when a field of ligands surrounds the metal ion, the orbital energies increase due to the repulsion between ligands and metal electrons.

In most transition metal complexes, the metal is surrounded by either six or four ligands, forming octahedral or tetrahedral structures. In both cases, the ligand field is not spherically symmetrical. Consequently, the impact on the d orbitals varies. In an octahedral complex, the metal occupies the center of the octahedron, with the ligands at the six corners.

Chemistry

The x, y, and z directions correspond to three adjacent corners of the octahedron, as illustrated in the figure. The lobes of the e.g., orbitals (d_{x2-y2} and d_{z2}) align with the x, y, and z axes, while the lobes of the t_{2g} orbitals (d_{xy} , d_{xz} , and d_{yz}) point between these axes. Therefore, the approach of six ligands along the x, y, z, -x, -y, and -z directions increase the energy of the dx2–y2 and dz2 orbitals (which align with the axes) more than it affects the d_{xy} , d_{xz} , and d_{yz} orbitals (which point between the axes). As a result, under the influence of an octahedral ligand field, the d orbitals split into two groups with differing energies. Instead of referring to the energy levels of isolated metal atoms, the difference in energy between these two sets of d orbitals is represented by the symbols Δ_0 or 10 Dq.



It follows that the e_g orbitals are +0.6 Δ_0 above the average level, and the t_{2g} orbitals

 $-0.4 \Delta_0$ below the average level.



Fig. Diagram of the energy levels of d -orbitals in a octahedral field

In the context of tetrahedral complexes, consider a regular tetrahedron that is geometrically connected to a cube. Within this cube, one atom resides at its center, while four of the cube's eight corners are occupied by ligands, as depicted in the figure. The directions x, y, and z correspond to the centers of the cube's faces.

The e.g., orbitals are oriented along the x, y, and z axes, which coincide with the centers of these faces.



Fig. Relation of tetrahedron to a cube

The approach of the ligands raised the energy of both sets of orbitals. The energy of the t_{2g} orbital raised most because they are closest to the ligands. This crystals field splitting is opposite to that in octahedral complexes. The t_{2g} orbitals are 0.4 Δ_t above the average energy of the two groups (the Bari centre) and the e_g orbitals are 0.6 Δ_t below the average level.



Free metal ion

(five degenerate d orbitals)

Fig Crystal field splitting of energy levels in a tetrahedral field

Stability of complexes

A coordination compound is created in a solution through the gradual introduction of ligands to a metal ion. Consequently, the formation of the complex ML_n (where M represents the central metal cation, L denotes a monodentate ligand, and n stands for the coordination number of the metal ion) is presumed to occur in a sequence of n consecutive steps.

$$M + L \rightleftharpoons ML; K_{1} = \frac{[ML]}{[M][L]}$$

$$M + L \rightleftharpoons ML_{2}; K_{2} = \frac{[ML_{2}]}{[ML][L]}$$

$$ML_{2} + L \rightleftharpoons ML_{3}; K_{3} = \frac{[ML_{3}]}{[ML_{3}][L]}$$

$$ML_{n-1} + L \rightleftharpoons ML_{n}; K_{n} = \frac{[ML \cdot]}{[ML_{n-1} \parallel L]}$$

 K_1 , K_2 , K_3 K_n are called stepwise stability constants. With a few exceptions, the values of successive stability constants decrease regularly from K_1 to K_n . The overall stability constant K is given as

$$M + nL \rightleftharpoons ML_n;$$

$$K = K_1 K_2 K_3 \dots K_n = \frac{[ML_r]}{[M][L]'}$$

The greater the overall stability constant value of a complex, the greater its stability. Conversely, values of 1/K, referred to as instability constants, elucidate the dissociation of the complex into a metal ion and ligands within the solution. The table provides the stability constant values for several complexes.

-	Stability	constants	of comp	olexes
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Complex	Stability constant
$[Cu(NH_3)_4]^{2+}$	$4.5 imes 10^{11}$
[Ag(NH ₃) ₂]+	1.6×10^{7}
[Co(NH ₃) ₆] ²⁺	1.12×10^{6}

Chemistry

[Co(NH ₃) ₆]+	5.0× 10 ³³
[AgCl ₂]-	1.11×10^{5}
[AgBr ₂]-	1.28×10^{7}
[Ag(CN) ₂] ⁻	1.0×10^{22}
[Cu(CN) ₄] ²⁻	$2.0 imes 10^{27}$
[Fe(CN) ₆] ³⁻	$7.69 imes 10^{43}$

COLOUR IN COORDINATION COMPOUNDS

Coordination compounds containing transition metals exhibit intriguing colors. According to the crystal field theory, these colors arise from d-d transitions of electrons influenced by ligands. The color of a substance results from the absorption of light at a specific wavelength within the visible part of the electromagnetic spectrum (ranging from 400 to 700 nm), while the remaining wavelengths are either transmitted or reflected. An object that absorbs all visible light appears black.

The mechanism of light absorption in coordination compounds involves photons with sufficient energy exciting the coordination entity from its ground state to an excited state. Consider the example of the Ti (III) ion in solution, such as $[Ti (H_2O)_6]^{3+}$. This forms a violet-colored octahedral complex, where, in the ground state, a single electron resides in the t_{2g} level. The next available state for transition is the empty e_g level. When light corresponding to the energy of yellow-green is absorbed by the complex, it excites the electron from the t_{2g} level to the e_g level. Consequently, the complex appears violet.

For copper (II) ions in solution, one of the d-electrons from the t_{2g} set (d_{xy} , d_{yz} , d_{xz} orbitals) may be imagined to get excited to the e_g set (orbitals). In this case, since high-energy light is transmitted, it implies that low-energy light (in the red region) is absorbed. In the case of copper (II) ions in aqueous solution, the energy gap Δ_t is relatively small. The table below illustrates the relationship between the wavelength of absorbed light and the observed color.

Relationship between the wavelength of light absorbed and the colour observed In some coordination entitles

Coordination entity	Wavelength of light	Colour of light	Colour of coordination	
-	absorbed (nm)	absorbed	entity	
[CoCl(NH ₃) ₅] ²⁺	535	Yellow	Violet	
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green	Red	
[Co(NH ₃) ₆] ³⁺	475	Blue	Yellow Orange	
[Co(CN0 ₆] ³⁻	310	Ultraviolet	Pale Yellow	
$[Cu(H_2O)_4]^{2+}$	600	Red	Blue	
[Ti(H ₂ O) ₆] ³⁺	498	Blue Green	Purple	

Note:

(a) In the absence of ligands, crystal field splitting does not take place, resulting in the substance having no color and appearing colorless.

For example;

- (i) removal of water from violet coloured complex [Ti(H₂O)₆]Cl₃ on heating makes it colourless,
- (ii) similarly anhydrous copper sulphate (CuSO₄) is white, but hydrated copper sulphate (CuSO₄.5H₂O) is blue coloured.
- (b) The nature of the ligand and the molar ratio of metal: ligands also influence the colour of the complex.

For example; in the pale green complex of $[Ni(H_2O)_6]$, the colour change is

observed when ethylenediamine is progressively added to it.

Molar ratio of en: Ni	Coloured obs erved
1:1	Pale blue
1:1	Blue/Purple
1:1	Violet

Note: Ruby is Al_2O_3 in which 0.5–1% Cr^{3+} ions (d³ electron system) are randomly distributed in the positions normally occupied by Al^{3+} . We may consider Cr(III) species as octahedral Cr(III) complexes incorporated into the alumina lattice; d-d transition of electron at these centres/points give rise to the colour (red).

Amerland is the mineral beryl ($Be_3Al_2Si_6O_{18}$) in which Cr^{3+} ions occupy octahedral sites, but in this case low energy corresponding to yellow red and blue is absorbed and light corresponding to green region is transmitted.

FACTORS AFFECTING STABILITY OF COMPLEX COMPOUNDS

- (i) The stability constant values exhibit considerable variation, primarily influenced by the characteristics of both the metal ion and the ligand. Generally, a higher charge density on the central ion corresponds to increased stability for its complexes.
- (ii) The ease with which a ligand can donate its lone pairs of electrons, and consequently the stability of the complexes it forms, is directly proportional to its basicity.
- **Ex.** The cyano and ammine complexes are far more stable than those formed by halide ions. This is due to the fact that NH₃ and CN⁻ are strong Lewis bases.
- (iii) The higher the oxidation state of the metal, the more stable is the complex. The charge density of Co^{3+} ion is more than Co^{2+} ion and thus, $[\text{Co}(\text{NH}_3)_6]^{3+}$ is more stable than $[\text{Co}(\text{NH}_3)_6]^{2+}$. Similarly, $[\text{Fe}(\text{CN})_6]^{3-}$ is more stable than $[\text{Fe}(\text{CN})_6]^{4-}$.
- (iv) Chelating ligands form more stable complexes as compared to monodentate ligands.